Rearrangements of 1-Cyclohexenylmethylenes and Their Relevance to the Mechanism of the Phenylcarbene Rearrangement†

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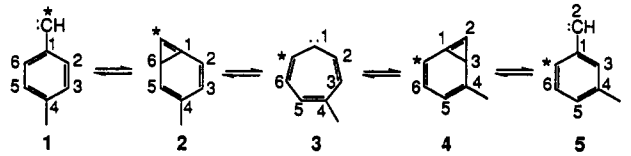
Received September 14, 1990

Gas-phase pyrolysis of 1-cyclohexenyldiazomethane (17) and (2-methyl-1-cyclohexenyl)diazomethane (36) leads to the generation of cyclohexenylmethylenes, 13 and 27, respectively, whose intramolecular rearrangement mechanisms can be inferred from the stable end products. These substituted vinylmethylenes undergo intramolecular π-addition, but apparently do not participate in an all-carbon Wolff rearrangement. The relevance of these results to the mechanism of the phenylcarbene rearrangement is discussed, and it is suggested that a π-route with a bicycloheptatriene-like transition state may operate. An attempt to generate 1,3-cyclohexadienylmethylene is described.

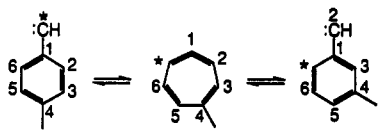
Introduction

There is considerable evidence that 1,2,4,6-cycloheptatetraenes are intermediates in the interconversion of isomeric phenylmethylenes ("phenylcarbenes").[1-4] When the facile thermal interconversion of phenylcarbenes was recognized in 1970,[5] bicycloheptatriene **2**, **4**, and cycloheptatrienylidene **3** intermediates were proposed, as shown below for the interconversion of *p*-tolylmethylene (**1**), and *m*-tolylmethylene (**5**).



1 **2** **3** **4** **5**

Semiempirical calculations have predicted that singlet cycloheptatrienylidene is not a minimum on the potential surface for c-C_7H_6, but that bicycloheptatriene is an intermediate in the rearrangement of singlet phenylmethylene to 1,2,4,6-cycloheptatetraene.[6] In their matrix-isolation studies of the interconversion of triplet phenylmethylenes, the Chapman group did not observe either bicycloheptatriene or cycloheptatrienylidene intermediates and have therefore presented mechanisms including only the intermediates that they did observe, e.g. cycloheptatetraenes, e.g., **6**, as shown below for the interconversion of *p*- and *m*-tolylmethylene (**1**–**5**).[1-4]



1 **6** **5**

Chapman has not proposed a mechanism for the rearrangement of phenylmethylene (**7**) to 1,2,4,6-cycloheptatetraene (**8**), a reaction that has little precedent in the chemistry of vinylcarbenes. Rearrangement of vinylcarbenes to allenes is rare,[7] while ring closure to cyclopropenes is well-known.[8]

Two discrete mechanisms can be considered for the rearrangement of phenylmethylene (**7**) to 1,2,4,6-cycloheptatetraene (**8**). It is the difficulty of testing these mechanistic suggestions that led to the experimental work reported here.

Both these mechanisms can be regarded as 2 + 2 cycloadditions. The first mechanism is an all-carbon version of the Wolff rearrangement, the σ-mechanism, in which a 1,2-carbon–carbon σ-bond shift occurs without significant participation by the aromatic π-electron system (Scheme I). In the second mechanism, the π-mechanism, the π-system interacts strongly with the carbene center, leading to either a transition state **9** that resembles a bicycloheptatriene or to a bicycloheptatriene intermediate **10**. If there is a bicycloheptatriene *intermediate*, formation of the cycloheptatetraene is a consequence of a six-electron process, an electrocyclic ring opening, following the 2 + 2 process. If the bicycloheptatriene structure represents a transition state, the electrocyclic ring opening and the 2 + 2 process are coupled.

Here we study the rearrangements of 1-cyclohexenylmethylenes, since they contain the minimum structural elements required for both versions of the phenylcarbene rearrangement mechanism presented above. For these molecules, product structures can distinguish between the suggested reaction pathways. It will be argued in the conclusion that these results are relevant to a discussion of the mechanism of the phenylcarbene rearrangement, although proof is not at hand that these molecules are reliable models for phenylcarbenes. What is being probed directly is the tendency to form a seven-membered cyclic allene **11** versus a [4.1.0]bicyclic cyclopropene **12** in the rearrangement of 1-cyclohexenylmethylene (**13**).

As shown in the scheme below, a σ-mechanism for the rearrangement of 1-cyclohexenylmethylene (**13**) is expected to form the allene, 1,2-cycloheptadiene (**11**) that could readily dimerize to a stable product **14**. Rearrangement of the carbene by intramolecular π-attack would lead to bicyclo[4.1.0]hept-6-ene (**12**), that is expected to rearrange to 1,3-cycloheptadiene (**15**) via cyclohept-2-enylidene (**16**).

Results and Discussion

1-Cyclohexenyldiazomethane (**17**) was generated in situ by heating an evacuated flask containing the tosylhydrazone sodium salt of 1-cyclohexene-1-carboxaldehyde (**18**) from room temperature to a temperature (68–110 °C) sufficient to decompose it. The liberated diazo compound

† This work was carried out with financial support from the U.S. National Science Foundation under Grant No. CHE-88-02677.

(1) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779.
(2) McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. H.; West, P. R. *Ibid.* **1987**, *109*, 2456.
(3) West, P. R.; Mooring, A. M.; McMahon, R. J.; Chapman, O. L. *J. Org. Chem.* **1986**, *51*, 1316.
(4) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1988**, *110*, 501.
(5) Baron, W. J.; Jones, M., Jr.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 4739.
(6) Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 6179.
(7) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3971.
(8) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971.

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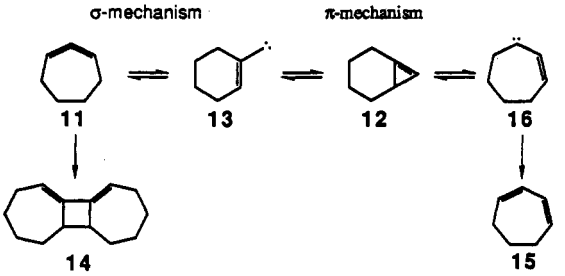
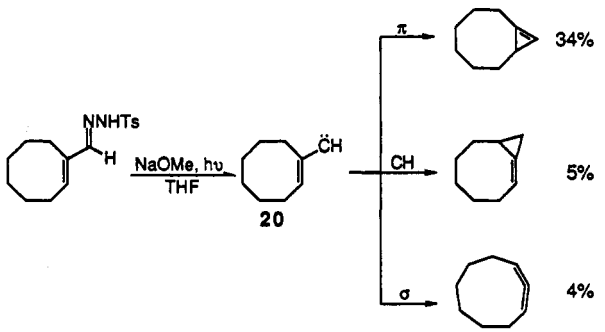


evaporated and passed through the pyrolysis zone, and the products were condensed in a trap cooled with liquid nitrogen. The onset of diazo compound pyrolysis and its termination were monitored by a slight pressure rise in the system (from 5 to ca. 50 μm) and its subsidence.

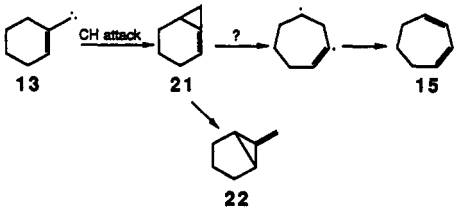
The products were 1,3-cycloheptadiene (15) and 4,5,6,7-tetrahydro-1*H*-indazole (19), whose yields obtained at various pyrolysis temperatures are given in Table I.

The major product under all conditions was pyrazole 19, which was presumably formed by cyclization of the diazo compound 17, followed by a 1,5-hydrogen shift, a process with considerable precedent.[9] The major process leading to the formation of 1,3-cycloheptadiene (15) can be presumed to be intramolecular attack of the carbene center on the π-system, the π-mechanism illustrated in Scheme II.

Stierman and Johnson have found that intramolecular attack by the carbene center of photochemically generated 1-cyclooctenylmethylene (20) on a C–H bond is a minor process accompanying π-attack, the major reaction, with the σ-mechanism also contributing to a small extent.[7,10]



In the thermal generation of 1-cyclohexenylmethylene (13) reported here, a minor contribution from an analogous intramolecular attack on a C–H bond, pictured below, has not been ruled out. The intermediate resulting from such a C–H attack, $\Delta^{1,2}$-bicyclo[4.1.0]heptene (21) has been shown, however, to yield 6-methylenebicyclo[3.1.0]hexane (22) upon pyrolysis. We did not find 22 as a product upon the thermal generation of 1-cyclohexenylmethylene, 13. Thus 21 may not have been formed, and in any case is unlikely to contribute to the formation of 1,3-cycloheptadiene (15) from 1-cyclohexenylmethylene (13).

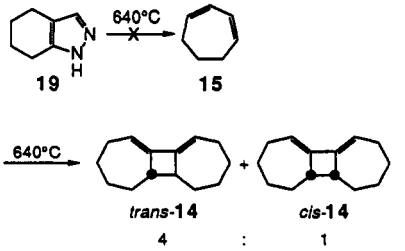


(9) Reference 8, p 22.
(10) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 2492.
(11) Kende, A. S.; Riecke, E. E. *J. Chem. Soc., Chem. Commun.* **1974**, 383.

Table I. Pyrolysis of 1-Cyclohexenyldiazomethane 17

mmol of precursor salt 19	% convn of precursor salt 18	temp, °C	% yield of cycloheptadiene 15	% yield of pyrazole 19
1	86	620	16	74
1	100	510	17 (18)	77 (82)
1	100	400	6	87
3	94	515	22	74

A control pyrolysis at 640 °C showed that the pyrazole 19 does not decompose at this temperature and is not converted into 1,3-cycloheptadiene (15). Another control experiment indicated that allene dimers 14 of 1,2-cycloheptadiene are fairly stable at the pyrolysis temperatures, although some trans–cis isomerization occurs.



This experiment did not speak to the question whether the allene, 1,2-cycloheptadiene (11), undergoes dimerization in the gas phase, but only whether the allene dimer 14, if formed, would survive.[12] It was also necessary to address the remote possibility that 1,2-cycloheptadiene (11) rearranges under the flow pyrolysis conditions to the observed product 1,3-cycloheptadiene (15). To demonstrate that the allene 11, if formed, would dimerize, it was necessary to generate it in the gas phase, apparently for the first time. Elimination of HCl from 1-chlorocycloheptene under flow-pyrolysis conditions at 640 °C failed, with quantitative recovery of the starting material.

1,2-Cycloheptadiene (11) was formed in the gas phase using the strategy employed by Wentrup for the six-membered cyclic allene 1,2-cyclohexadiene.[13]

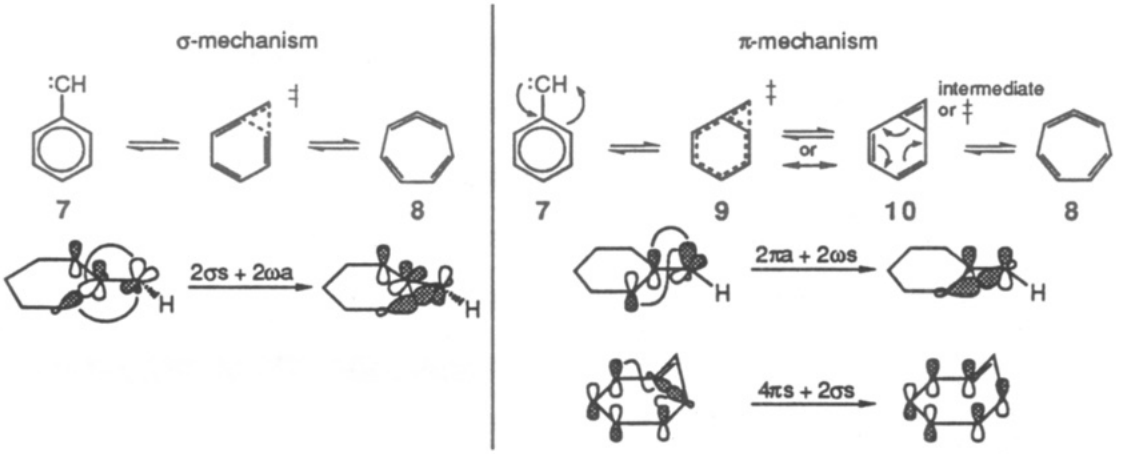
Elimination of HCl in the flow pyrolysis of norcarane carboxylic acid chloride (23) led to the ketene 24 that in turn lost carbon monoxide, giving the carbene norcaranylidene (25) whose rearrangement gave the desired 1,2-cycloheptadiene (11). Dimerization products 14 and their HCl adducts 26 were obtained in overall yield of 25%. The maximum yield of 1,3-cycloheptadiene (15) from this experiment was less than 0.5%. Thus, this control experiment establishes that rearrangement of 1-cyclohexenylmethylene (13) does not yield cyclic allene 1,2-cycloheptadiene (11), and that the 1,3-cycloheptadiene product 15 observed from rearrangement of 1-cyclohexenylmethylene (13) did not arise from this cyclic allene.

As seen from the results of Table I, an increase in the pyrolysis temperature of the diazo compound 17 from 400 to 510 °C leads to an increase in the yield of the cycloheptadiene 15 at the expense of the pyrazole 19, suggesting that liberation of the carbene from the diazo compound has a higher activation energy than cyclization.

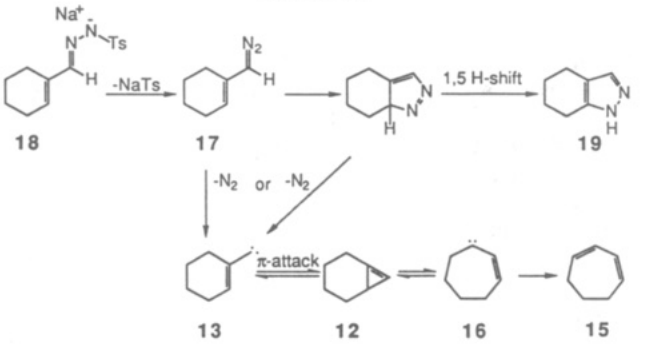
Control experiments demonstrated that 1-cyclohexenyldiazomethane (17) was reaching the pyrolysis hot zone and thus pyrazole formation was an unavoidable product of the pyrolysis. To avoid pyrazole formation it

(12) Wentrup and co-workers (ref 13) have shown that upon generation of 1,2-cyclohexadiene in a gas-phase flow system, dimerization occurs upon warming the trap in which the cyclic allene was frozen.
(13) Wentrup, C.; Gross, G.; Maquestiau, A.; Flammang, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 542.

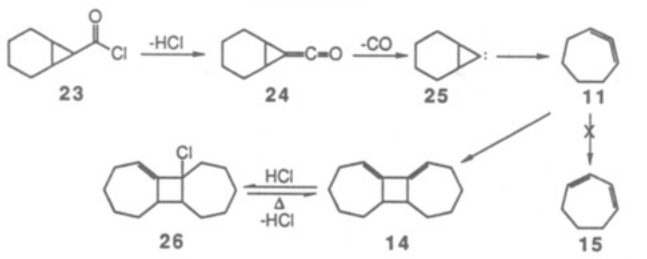
Scheme I



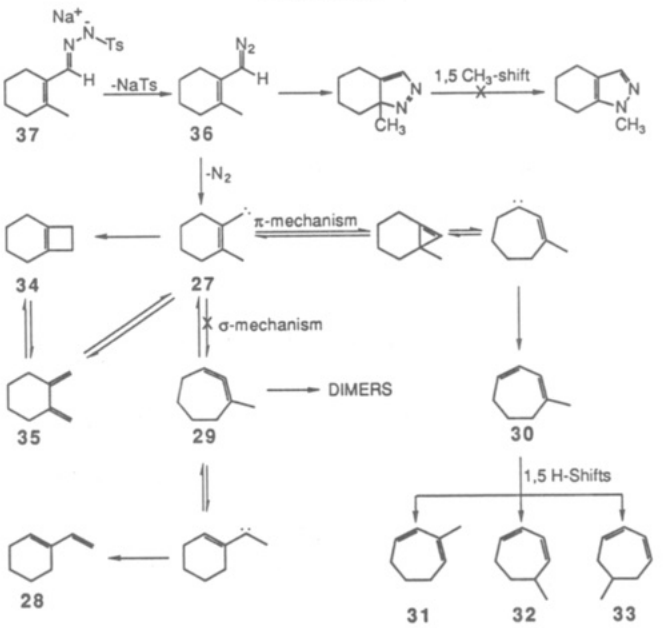
Scheme II



Scheme III



Scheme IV



is necessary to use a different carbene source or instead to modify the structure of the diazo compound to discourage cyclization. The latter strategy was chosen, and (2-methyl-1-cyclohexenyl)methylene (**27**) was generated.

As shown in Scheme IV below, a σ-mechanism for the rearrangement of (2-methyl-1-cyclohexenyl)methylene (**27**) is expected to lead to stable products different from those originating from intramolecular π-attack. The former process is expected to lead to the isolation of 1-vinylcyclohexene (**28**) or to dimers of the allene 1-methyl-1,2-cycloheptadiene (**29**), while the latter rearrangement is expected to produce 1-methyl-1,3-cycloheptadiene (**30**) and its isomers **31–33** that result from facile 1,5-hydrogen shifts.[14] The price paid for the presence of the methyl group was an additional reaction channel for (2-methyl-1-cyclohexenyl)methylene (**27**), formation of a cyclobutene derivative **34**, expected to undergo ring opening to 1,2-dimethylenecyclohexane (**35**). A similar ring opening has been observed for benzocyclobutene.[15,16]

A further advantage of (2-methyl-1-cyclohexenyl)diazomethane (**36**) over 1-cyclohexenyldiazomethane (**17**), in addition to the expected suppression of pyrazole formation, was the availability of intramolecular stabilization pathways for both the cyclic allene **29** resulting from the σ-mechanism and the bicyclic cyclopropene resulting from intramolecular π-attack.

The diazo compound **36** was generated in situ by gentle pyrolysis of the tosylhydrazone sodium salt of 2-methyl-1-cyclohexenecarboxaldehyde (**37**). When the liberated diazo compound **36** was evaporated through the pyrolysis hot zone at 500 °C, the products obtained consisted entirely of hydrocarbons, with a quantitative yield of C_8H_{12} isomers. Of these, 24% consisted of 1,2-dimethylenecyclohexane (**35**), resulting from intramolecular attack of the (2-methyl-1-cyclohexenyl)methylene (**27**) carbene center on the methyl group. All the other products were isomeric methyl-1,3-cycloheptadienes **30–33**, presumably resulting from initial intramolecular π-attack by the carbene center.

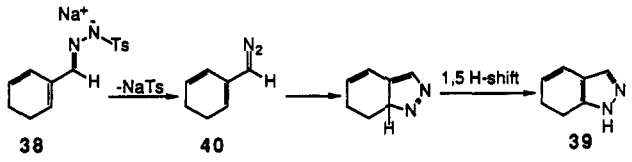
No 1-vinylcyclohexene (**28**) or allene dimers, the expected stable products of the σ-mechanism, were found. As a control it was demonstrated that a 0.4% yield of

(14) Miranov, V. A.; Chizhof, O. S.; Kimelfeld, I. M.; Akhrem, A. A. *Tetrahedron Lett.* **1969**, 499.

(15) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683.

(16) Chapman, O. L.; Tsou, U.-P. E.; Johnson, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 553.

Scheme V



1-vinylcyclohexene (28) would have been detected readily. Thus it is clear that (2-methyl-1-cyclohexenyl)methylene (27) and 1-cyclohexenylmethylene (17) both undergo rearrangement predominantly via an intramolecular π-addition, with no indication of the occurrence of the σ-mechanism.

It was hoped to generate 1,5-cyclohexadienylmethylene in an analogous manner from the tosylhydrazone sodium salt of 1,5-cyclohexadiene-1-carboxaldehyde (38). This carbene resembles phenylmethylene more closely both in geometry and in the nature of the bond that would migrate in a σ-mechanism. Unfortunately, as shown in Scheme V, only the pyrazole 6,7-dihydro-1*H*-indazole (39) was obtained, in 87% yield, with no trace of hydrocarbon products. A control experiment indicated that the diazo compound 40 is rather unstable, and a much lower proportion reaches the pyrolysis hot zone. Clearly a different precursor would be required to study this carbene.

Concluding Remarks

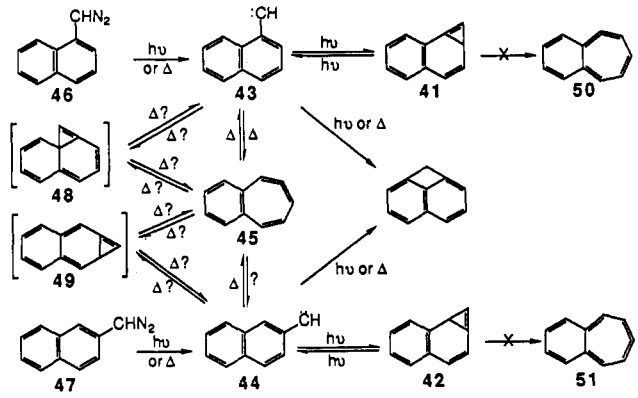
For the two 1-cyclohexenylmethylenes 13 and 27 studied here, the favored pathway for intramolecular rearrangement is attack of the carbene center on a π-bond. There is no sign of rearrangement via a σ-mechanism, involving a migration of a carbon–carbon σ-bond as a primary process. For 1-cyclohexenylmethylene (13) and (2-methyl-1-cyclohexenyl)methylene (27), these two pathways can be distinguished, because different stable end products are expected from the reaction sequences initiated by the carbene rearrangement.

As indicated in the introduction, similar pathways can be written for the rearrangement of phenylmethylene (7) to 1,2,4,6-cycloheptatetraene (8). Does the π-mechanism, with a bicycloheptatriene intermediate 10 or transition state 9, operate for the rearrangements of phenylmethylenes as it does for the rearrangements of 1-cyclohexenylmethylenes studied here? Chapman has not observed bicycloheptatriene intermediates in the rearrangements of phenylmethylenes under frozen matrix conditions and has found no reason to include them in his proposed reaction sequence.[1]

Bicycloheptatriene derivatives 41 and 42 were, however, observed by Chapman when naphthylcarbenes 43 and 44 were generated in frozen matrices, while a cyclic allene 45 was only detected upon matrix isolation of the pyrolysate of napthyldiazomethanes 46 and 47.[3] As indicated in Scheme VI, the cyclic allene 45 observed by Chapman in the naphthyldiazomethane pyrolysis experiments is not the isomer that would arise from electrocyclic ring opening of either of the energetically favored bicycloheptatriene derivatives 41 and 42. In his report on the rearrangements of napthylmethylenes 43 and 44, Chapman restates his view that phenylmethylene bypasses a bicycloheptatriene intermediate in its ring expansion to a cyclic allene. One can however, interpert Chapman's results on the rearrangements of naphthylmethylenes 43 and 44 as being in accord with bicycloheptatriene intermediates or transition states 48 and 49 in the ring expansion of naphthylmethylenes to benzocycloheptatetraene 45.

For the naphthylcarbenes 43 and 44 studied by Chapman, ring expansion to a cyclic allene clearly is a less facile

Scheme VI



process than intramolecular π-addition to form the observed bicycloheptatriene derivatives 41 and 42. This can be understood if ring expansion to a cyclic allene proceeds via π-attack.

Cyclic allene 45, whose formation from naphthylcarbenes 43 and 44 was observed by Chapman in pyrolysis experiments, can be formed by π-attack concomitant with, or followed by, an electrocyclic ring opening, only at the expense of intermediates or transition states 48 and 49 that have sacrificed all the aromaticity of the naphthalene π-system. The alternative π-attack for both naphthyl carbenes 43 and 44 gives the benzobicycloheptatrienes 41 and 42 observed by Chapman in matrix photolyses. The observed bicycloheptatrienes 41 and 42 would form, upon electrocyclic ring opening, cyclic allenes 50 and 51 that have forfeited all the aromaticity of napthalene. These have been calculated by Jones to lie some 40 kcal/mol higher than the isomer 45 detected by Chapman in a pyrolysis experiment.[17]

In the case of phenylmethylene 7, rearrangement to the cyclic allene 8 via a σ-mechanism should have a similar barrier to the analogous process in the naphthylcarbene series. From Chapman's work, however, one can infer a lower barrier for rearrangement of arylcarbenes to cyclic allenes in the phenylmethylene series than in the naphthylmethylenes. This is understandable if a π-mechanism operates for the arylcarbene to cyclic allene rearrangement, since a lower energy cost must be paid in lost aromaticity in the case of the phenylmethylenes than for naphthylmethylenes.

Ring closure of unsubstituted singlet vinylmethylene to cyclopropene has been calculated by Yoshimine and coworkers using ab initio methods to have a barrier less than 5 kcal/mol.[18] Both ring closure of phenylmethylene (7) to bicycloheptatetraene (10) and the electrocyclic ring opening of 10 to cycloheptatetraene (8) have been calculated by Dewar to have a lower barrier.[6] The bicycloheptatriene structure 10 may be a transition state 9 and not an intermediate. The coupling of an electrocyclic ring opening to intramolecular π-attack by phenylmethylene allows us to understand why phenylmethylene undergoes facile rearrangement to a cyclic allene, while naphthylmethylenes do so only under forcing conditions, and the 1-cyclohexenylmethylenes 13 and 27 studied in this work show no signs of allene formation.

Thus, while the relevance of the rearrangements of the 1-cyclohexenylmethylenes 13 and 27 studied here to the elucidation of the chemistry of phenylmethylenes is cer-

(17) Balci, M.; Winchester, W. R.; Jones, W. M. *J. Org. Chem.* **1982**, *47*, 5180.
(18) Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 2785.

tainly not proven, the results reported here do seem to lend some support to the view that the phenylcarbene rearrangement follows a π-attack mechanism.

Experimental Section

General Procedures. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN. Proton magnetic resonance spectra were recorded on a Varian 300-XL NMR spectrometer at 300 MHz. Chemical shifts are reported as δ values measured in ppm downfield from Me_4Si, used as an internal reference. Infrared spectra were recorded on a Perkin-Elmer 283B infrared spectrometer, calibrated against the 1601.3-cm^{-1} band of polystyrene. Ultraviolet spectra were recorded on a Cary-219 ultraviolet spectrometer. Mass spectra were recorded on a Finnigan 3200 GC/MS spectrometer operating at an ionizing voltage of 70 eV and calibrated against perfluoroalkane. FAB mass spectra were recorded on a VG ZAB-SE instrument. Gas chromatograms were recorded on a home-made instrument[19] employing Gow-Mac Code 13-002 dual rhenium-tungsten filaments as thermal conductivity detectors. A Varian model 2740-10 gas chromatograph with a flame ionization detector was also employed.

1-Cyclohexene-1-carboxaldehyde was synthesized by the method of Brandsma and Verkruijsse (4.7 g, 62% yield, bp 67–70 °C (10–12 Torr), lit. bp 66 °C (12 Torr)):[20] ^{1}H NMR ($CDCl_3$) δ 1.55–1.75 (m, 4 H, C4-H, C5-H), 2.15–2.25 (m, 2 H, C3-H or C6-H), 2.30–2.40 (m, 2 H, C3-H or C6-H), 6.80–6.85 (m, 1 H, C2-H), 9.45 (s, 1 H, CH=O); ^{13}C NMR ($CDCl_3$) δ 21.4, 21.5, 22.2, 26.6, 142.0, 152.2, 194.4; MS *m/e* (relative intensity) 111 (5.7), 110 (P, 69), 95 (43), 91 (16), 81 (100), 79 (90), 77 (35), 67 (38), 54 (16), 53 (35), 51 (17).

2-Methyl-1-cyclohexene-1-carboxaldehyde was synthesized by the method of Harding and Ligon (6.3 g, 45% yield, bp 84–86.5 °C (10 Torr), lit. bp 90 °C (0.15 Torr)):[21] ^{1}H NMR ($CDCl_3$) δ 1.50–1.70 (m, 4 H, C4-H, C5-H), 2.10–2.30 (s and m, 7 H, C2-Me and C3-H, C6-H), 10.20 (s, 1 H, CH=O).

1,5-Cyclohexadiene-1-carboxaldehyde was synthesized by the method of Cohen et al. (2.1 g, 52% yield, bp 71–72 °C (14 Torr), lit. bp 65 °C (16 Torr)):[22] ^{1}H NMR ($CDCl_3$) δ 2.20–2.35 (m, 2 H, C3-H or C4-H), 2.40–2.60 (m, 2 H, C3-H or C4-H), 5.96 (dt, 1 H, J_d = 9.8 Hz, J_t = 4.5 Hz, C5-H), 6.37 (dq, 1 H, J_d = 9.8 Hz, J_q = 1.6 Hz, C6-H), 6.74 (t, 1 H, J_t = 4.6 Hz, C2-H), 9.35 (s, 1 H, CH=O).

Bicyclo[4.1.0]heptane-7-carbonyl chloride (23) was synthesized by the method of Hodgkins and Flores (2.9 g, 11.4% yield based on ethyl diazoacetate, bp 107–109 °C (13 Torr), lit. bp 108 °C (15 Torr)):[23] ^{1}H NMR ($CDCl_3$) δ 1.10–1.40 (m, 4 H, C3-H, C4-H), 1.70–1.85 (m, 3 H, C1-H, C6-H, C7-H), 1.85–2.00 (m, 4 H, C2-H, C5-H); ^{13}C NMR ($CDCl_3$) δ 20.8, 23.0, 28.0, 36.5, 174.0.

***trans*-Tricyclo[7.5.0.0^{2,8}]tetradeca-7,9-diene (14)** was synthesized by the method of Bottini et al. (4.1 g, 57% yield, bp 122.5–124 °C (4 Torr), lit. bp 123–137 °C (4 Torr)):[24] ^{1}H NMR[25] ($CDCl_3$) δ 1.20–1.50, 1.75–2.25 (m, 16 H, CH_2), 2.50 (broad d, 2 H, cyclobutane CH), 5.75–5.85 (m, 2 H, olefinic CH); ^{13}C NMR[25] ($CDCl_3$) δ 29.0 (CH_2), 29.8 (CH_2), 31.1 (CH_2), 33.4 (CH_2), 50.0 (cyclobutane CH, J_{CH} = 132.8 Hz), 119.0 (olefinic CH, J_{CH} = 154.0 Hz), 146.0 (olefinic C); IR[25] (neat NaCl plates, cm^{-1}) 3017, 2901, 2842, 2677, 1442, 1354, 1267, 1214, 1154, 1123, 1104, 1040, 966, 875, 840, 794, 746; UV[24] (2,2,4-trimethylpentane) λ_{max} nm (ϵ) 268 (shoulder, 12 500), 258 (16 600), 251 (shoulder, 14 500) (lit. 270 (shoulder), 260 (17 500), 254 (shoulder)); MS *m/e* (relative intensity) 189 (2.3), 188 (P, 14), 146 (15), 145 (40), 132 (15), 131 (52), 129 (16), 128 (14), 119 (22), 118 (17), 117 (56), 115 (28), 105 (41), 104 (15), 93 (16), 92 (22), 91 (100), 79 (40), 78 (18), 77 (40), 67 (18), 65 (22).

1-Vinylcyclohexene (28) was synthesized by the method of Robins and Walker (4.25 g, 35.2% yield, bp 142–145 °C, lit. bp 77 °C (17 Torr)):[26] ^{1}H NMR[27,28] ($CDCl_3$) δ 1.50–1.80 (m, 4 H, ring CH_2's at C3 and C4), 2.00–2.25 (m, 4 H, ring CH_2's at C2 and C5), 4.88 (d, 1 H, ABX, J_{AX} = 10.8 Hz, terminal olefinic ZCH, geminal CH_2 coupling not resolved), 5.06 (d, 1 H, ABX, J_{BX} = 17.6 Hz, terminal olefinic ECH, geminal CH_2 coupling not resolved), 5.80 (m, 1 H, C6-H), 6.35 (dd, 1 H, ABX, J_{AX} = 10.8 Hz, J_{BX} = 17.6 Hz, vinyl CH=C); ^{13}C NMR[27] ($CDCl_3$) δ 22.5 (CH_2) 23.0 (CH_2), 24.5 (CH_2), 26.0 (CH_2), 110.0 (CH_2), 130.0 (CH), 136.0 (C), 141.0 (CH).

1-Chlorocycloheptene was synthesized by the method of Brandsma and Verkruijsse (27.6 g, 53% yield, bp 62–63 °C (16 Torr), lit. bp 50 °C (12 Torr)):[20] ^{1}H NMR ($CDCl_3$) δ 1.50–1.80 (m, 6 H, C4-H, C5-H, C6-H), 2.10 (dd, 2 H, J_d = 6.5, 11.0 Hz, C3-H), 2.55 (distorted t, 2 H, J_t = 5.5 Hz, C7-H), 6.00 (t, 1 H, J_t = 6.5 Hz, C2-H); ^{13}C NMR ($CDCl_3$), δ 27.3 (CH_2), 28.1 (CH_2) 29.3 (CH_2), 31.8 (CH_2), 40.2 (CH_2), 130.0 (olefinic CH), 136.3 (olefinic CCl).

Preparation of Tosylhydrazones. Tosylhydrazine was added to 10–15 mL of MeOH in a 25-mL round-bottom flask maintained at 0 °C under nitrogen. The aldehyde (ca. 1 equiv) was added all at once while the mixture was stirred with a magnetic stirring bar. The solids dissolved in 1–20 min. After an additional 5–45 min, a solid precipitated in most cases. If TLC analysis indicated that reaction was not occurring at room temperature, heat was applied, or HCL gas was bubbled into the reaction mixture. In some cases precipitation must be induced. The tosylhydrazone powder or crystals were filtered and dried over P_2O_5.

1-Cyclohexene-1-carboxaldehyde tosylhydrazone was synthesized by the method described above from 3.9 g of tosylhydrazine and 2.3 g of 1-cyclohexene-1-carboxaldehyde (4.0 g, 69% yield, mp 119–120 °C): ^{1}H NMR ($CDCl_3$) δ 1.55–1.70 (m, 4 H, cyclohexene C4-H, C5-H), 2.10–2.25 (m, 4 H, cyclohexene C3-H, C6-H), 2.45 (s, 3 H, tosyl Me), 5.95–6.05 (m, 1 H, cyclohexene C2-H), 7.30 (d, 2 H, J_{AB} = 8.2 Hz, tosyl C3-H, C5-H), 7.36 (s, 1 H, CH=N), 7.85 (d, 2 H, J_{AB} = 8.2 Hz, tosyl C2-H, C6-H), 8.00 (broad s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 21.8, 21.9, 22.4, 23.3, 26.2, 128.0, 129.6, 135.0, 135.3, 137.6, 143.9, 152.0; FAB MS *m/e* (relative intensity) 280 (4.2), 279 (P + H, 23), 123 (19), 91 (17), 79 (92), 78 (65), 63 (100), 62 (17), 61 (50). Anal. Calcd for $C_{14}H_{18}N_2O_2S$: C, 60.43; H, 6.47. Found: C, 60.44; H, 6.39.

2-Methyl-1-cyclohexene-1-carboxaldehyde tosylhydrazone was synthesized as described above from 3.45 g (18.6 mmol) of tosylhydrazine and 2.30 g (18.6 mmol) of 2-methyl-1-cyclohexene-1-carboxaldehyde (2.7 g, 50% yield, mp 135–137 °C dec): ^{1}H NMR ($CDCl_3$) δ 1.50–1.70 (m, 4 H, cyclohexene C4-H, C5-H), 1.75 (s, 3 H, cyclohexene C2 Me), 2.00–2.10 (m, 2 H, cyclohexene C3-H or C6-H), 2.10–2.20 (m, 2 H, cyclohexene C3-H or C6-H), 2.40 (s, 3 H, tosyl Me), 7.30 (d, 2 H, J_{AB} = 8.3 Hz, tosyl C3-H, C5-H), 7.85 (d, 2 H, J_{AB} = 8.3 Hz, tosyl C2-H, C6-H), 7.95 (s, 1 H, CH=N), 8.35 (broad s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 19.5, 22.0, 22.7, 23.0, 24.0, 33.5, 127.5, 128.7, 130.0, 135.6, 142.8, 144.0, 149.0. Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.64; H, 6.85. Found: C, 61.45; H, 6.87.

1,5-Cyclohexadiene-1-carboxaldehyde tosylhydrazone was synthesized as above from 2.60 g (14.0 mmol) of tosylhydrazine and 1.50 g (14.0 mmol) of 1,5-cyclohexadiene-1-carboxaldehyde (3.15 g, 81% yield, mp 135–142 °C dec): ^{1}H NMR ($CDCl_3$) δ 2.10–2.35 (m, 4 H, cyclohexadiene C3-H, C4-H), 2.40 (s, 3 H, tosyl Me), 5.91 (dt, 1 H, J_d = 9.8 Hz, J_t = 4.6 Hz, cyclohexadiene C5-H), 5.97 (t, 1 H, J_t = 4.7 Hz, cyclohexadiene C2-H), 6.40 (dq, 1 H, J_d = 9.8 Hz, J_q = 1.5 Hz, cyclohexadiene C6-H), 7.30 (d, 2 H, J_{AB} = 8.5 Hz, tosyl C3-H, C5-H), 7.85 (d, 2 H, J_{AB} = 8.5 Hz, tosyl C2-H, C6-H), 8.10 (s, 1 H, CH=N); ^{13}C NMR ($CDCl_3$) δ 22.0, 22.5, 24.0, 122.0, 128.0, 130.0, 132.0, 135.0, 136.0, 144.0, 150.0. Anal. Calcd

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for $C_{14}H_{16}N_2O_2S$: C, 60.87; H, 5.80. Found: C, 58.86; H, 5.56.

Preparation of Tosylhydrazone Sodium Salts. NaH (50% oil by wt) was weighed into a vial containing 1–3 mL of dry hexane. The mixture was swirled, and the NaH was allowed to settle. The hexane was removed and replaced with dry THF (distilled from Na). This mixture was swirled, and the resulting suspension was pipetted into a 25-mL round-bottom flask and cooled to 0 °C under nitrogen. The aldehyde tosylhydrazone dissolved in 1–3 mL of dry THF was transferred by syringe all at once into the flask. After 5–15 min a precipitated formed, and the THF was removed on a rotary evaporator, avoiding contact with water vapor. The tosylhydrazone sodium salt coated the sides of the flask, and the last traces of THF were removed upon evacuation to ca. 5 μm for 24–72 h on a vacuum line.

Pyrolysis of the Sodium Salt of 1-Cyclohexene-1-carboxaldehyde Tosylhydrazone (18). A flask whose walls were coated with sodium salt of 1-cyclohexen-1-carboxaldehyde tosylhydrazone (1–3 mmol, assuming total conversion) was attached via an O-ring joint to the pyrolysis apparatus. This consisted of a 7-mm i.d. Pyrex tube with a 90° bend. The flask containing the starting material was attached to a 7-cm vertical section, and a 20-cm horizontal section served as the pyrolysis hot zone. Heat was applied by passing current through 0.0253-in. Chromel A wire that was wound over a layer of asbestos paper that surrounded the hot zone. Temperature was measured with a iron-constantan thermocouple inserted between the asbestos layer and the Pyrex flow tube. The heating wire was embedded in a mixture of alundum cement and sodium silicate and covered with Zetex insulation. A 90° bent adapter led from the pyrolysis zone to an efficient trap constructed from two concentric tubes, the inlet of 9-mm i.d. Pyrex tubing, the outside tube, 17-mm i.d. cooled with liquid N_2. The outlet of the trap was connected to a vacuum line, and pressure was monitored with a calibrated thermocouple vacuum gauge. Both the starting material reservoir and the product trap were weighed to 10^{-4} g before an experiment.

At the beginning of the pyrolysis experiment the system was evacuated to a pressure of 5 μm. The hot zone was then heated to the pyrolysis temperature over a 2-h period. Then the product trap was cooled with liquid N_2, and the starting material reservoir was immersed in an oil bath and heated over a 1–2-h period to the temperature, 60–110 °C, required to liberate diazo compound from the tosylhydrazone sodium salt. The diazo compound evaporated and passed through the pyrolysis hot zone. The liberation of diazo compound was monitored by the increase in pressure from 5 μm to a maximum of 15–45 μm. The fall in pressure back to its initial value of 5 μm signalled the completion of the reaction.

At the end of the pyrolysis the outside of the starting material reservoir was carefully cleaned, and the flask weighed to 10^{-4} g in order to determine the weight of the liberated diazo compound from the weight loss during the experiment. The product trap was allowed to warm to room temperature under a nitrogen atmosphere, its outside carefully cleaned, and its weight determined to 10^{-4} g. The products were removed from the trap by washing with 1–2 mL of $CDCl_3$, and ^1H NMR spectra were recorded for the crude reaction mixture. While in one case product yields were determined by integration of the spectrum of an unseparated reaction mixture, yields were generally obtained by gas chromatography (10% OV-17 on ABS-Anakrom, 40–50 mesh, 10-ft by $^1/_4$-in.). Product yields from pyrolyses at 400, 510, and 620 °C are reported in Table I.

The same column was employed for micropreparative separations, and the pure components were characterized. 1,3-Cycloheptadiene (15): ^1H NMR[29] ($CDCl_3$) δ 1.90–1.95 (m, 2 H, C6-H), 2.15–2.20 (m, 4 H, C5-H, C7-H), 5.75–5.85 (m, 4 H, C1-H, C2-H, C3-H, C4-H); MS *m/e* (relative intensity) 95 (0.91), 94 (P, 12), 93 (4.0), 91 (9.4), 77 (20), 74 (83), 59 (100). 4,5,6,7-Tetrahydro-1*H*-indazole (19): ^1H NMR[30a,b] ($CDCl_3$) δ 1.78 (m, 4 H, C5-H, C6-H), 2.54 (t, 2 H, J_t = 6.1 Hz, C4-H or C7-H), 2.68 (t, 2 H, J_t = 6.1 Hz, C4-H or C7-H), 7.30 (s, 1 H, C3-H), 12.05 (s, 1 H, NH); ^{13}C NMR[30a] ($CDCl_3$) δ 20.6, 22.2, 23.3, 23.6, 115.0, 132.0, 143.0; IR (KBr, cm^{-1}) 3300–2200 (NH), 1436.5, 1370.3, 1331.4, 1281.6, 1233.5, 1163.6, 1054.3, 953.4, 848.9, 791.5; MS *m/e* (relative intensity) 123 (2.0), 122 (P, 28), 95 (14), 94 (100), 93 (12).

Pyrolysis of 4,5,6,7-Tetrahydro-1*H*-indazole (19). 4,5,6,7-Tetrahydro-1*H*-indazole (83.6 mg, 0.69 mmol) was placed in the starting material reservoir of the pyrolysis apparatus and the system evacuated to 6 μm. When the hot zone had been heated to 640 °C, the indazole was sublimed into the pyrolysis zone by heating the reservoir over a $2^1/_4$-h period slowly up to 152 °C. During this period the pressure rose by ca. 0.5 μm and returned to its initial value; 93% of the initial indazole sublimed from the reservoir and was quantitatively recovered, unchanged.

Pyrolysis of *trans*-Tricyclo[7.5.0.0^{2,8}]tetradeca-7,9-diene (14). Freshly distilled *trans*-tricyclo[7.5.0.0^{2,8}]tetradeca-7,9-diene (0.2360 g, 1.26 mmol) was placed in the starting material reservoir of a pyrolysis apparatus differing from the one described above only in the length of the hot zone (24 vs 20 cm) and in having an unheated right-angle adapter tube between the reservoir and the pyrolysis zone. With the starting material frozen at −196 °C the system was evacuated to 6 μm and the pyrolysis zone was heated to 640 °C. The reservoir was allowed to warm to room temperature and was then slowly heated over a $1^1/_4$-h period to 90 °C with an oil bath. During the experiment the pressure increased a maximum of 0.5 μm before returning to its initial value. A 95.4% yield was obtained of a 4.0:1.0 mixture of *trans*- and *cis*-tricyclo[7.5.0.0^{2,8}]tetradeca-7,9-diene. These isomers could be separated by gas chromatography. The cis isomer was identified by the similarity of its spectroscopic data and those of the trans isomer described above: ^1H NMR ($CDCl_3$) δ 1.10–1.50 and 1.60–2.30 (m, 16 H, CH_2), 2.88 (broad d, 2 H, J_d = 10.3 Hz, cyclobutane CH), 5.83 (m, 2 H, olefinic CH); ^{13}C NMR ($CDCl_3$) δ 27.8 (CH_2), 28.6 (CH_2), 29.5 (CH_2), 31.7 (CH_2), 44.4 (cyclobutane CH), 119.6 (olefinic CH), 147.3 (olefinic C); UV (2,2,4-trimethylpentane) λ_{max} nm (ε) 268 (12500), 258 (16600), 251 (14500); MS *m/e* (relative intensity) 189 (1.6), 188 (P, 12), 146 (14), 145 (38), 132 (15), 131 (50), 129 (14), 128 (14), 119 (23), 118 (16), 117 (55), 115 (28), 105 (43), 104 (15), 93 (18), 92 (24), 91 (100), 77 (39), 67 (18), 65 (22).

Pyrolysis of 1-Chlorocycloheptene. Freshly distilled 1-chlorocycloheptene (0.2680 g, 2.06 mmol) was placed in the reservoir of the pyrolysis apparatus described immediately above, together with a magnetic stirring bar, and frozen to −196 °C. The system was evacuated to 6 μm and the pyrolysis zone heated to 625 °C. The 1-chlorocycloheptene was allowed to warm to room temperature and evaporate through the hot zone over $^1/_4$ h. The pressure rose by 0.5 μm before dropping to its initial value; 99.5% of the 1-chlorocycloheptene was found in the product trap, completely unchanged.

Pyrolysis of bicyclo[4.1.0]heptane-7-carbonyl chloride (23) was carried out as described above for 1-chlorocycloheptene. During the course of the 90-min flow pyrolysis, the pressure rose from an initial value of 32 μm to a maximum of 115 μm when the reservoir was heated to 49 °C. It then dropped to its initial value. Analysis of the reaction mixture by gas chromatography revealed a <0.6% yield of a product with the same retention time as 1,3-cycloheptadiene and a 2.3% yield of an unidentified lower boiling product. The major product detected by gas chromatography was ca. 25% yield of *trans*-tricyclo[7.5.0.0^{2,8}]tetradeca-7,9-diene (14), accompanied by two minor products of similar retention time. The ^1H NMR spectrum of the crude pyrolysate does not, however, indicate the presence of the allene dimer, which is liberated upon injection into the vapor chromatograph. These results can be explained by reversible addition to the allene dimer of the HCl formed in the initial step of the reaction.

Pyrolysis of the Sodium Salt of 2-Methyl-1-cyclohexene-1-carboxaldehyde Tosylhydrazone (37). The procedure was similar to that for the pyrolysis of the sodium salt of 1-cyclohexene-1-carboxaldehyde tosylhydrazone (18) described above: 2.05 mmoles of sodium salt were pyrolized, assuming quantitative conversion of the tosylhydrazone to its sodium salt. The initial pressure was 7.5 μm, and the pyrolysis zone was heated to 500 °C. The reservoir was heated from 35 to 102 °C over 106 min, and the pressure rose to a maximum of 155 μm before falling back to 7.5 μm. The experiment was repeated. The conversion of starting sodium salt was 72.3% and 94.3%, respectively, in the two runs as determined from weight loss, and 98.3% and 91.8%

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as determined by ^1H NMR assay of the lithium toluene sulfinate formed. The total yields of C_8H_{12} isomers detected by gas chromatography were 92% and 101% in the two runs, respectively.

The pyrolysis products were analyzed and separated by gas chromatography on three columns of differing polarity. 1,2-Dimethylenecyclohexane (35) was separated from the other products by 10% OV-17 on Chromosorb W. On 20% SE-30 on Chromosorb P an inseparable mixture of 5-methyl-1,3-cycloheptadiene (32) and 6-methyl-1,3-cycloheptadiene (33) was separated from a mixture of 1-methyl-1,3-cycloheptadiene (30) and 2-methyl-1,3-cycloheptadiene (31). The latter mixture was separated by 10% Carbowax on Chromosorb W. The following individual yields were determined in the two runs: 1,2-dimethylenecyclohexene (35), 24.2% and 13.5%; 5-methyl-1,3-cyclohexadiene (32), 13.1% and 9.8%; 6-methyl-1,3-cyclohexadiene (33), 12.6% and 6.8%. In these two runs the sum of the yields of the 1-methyl-1,3-cyclohexadiene (30) and 2-methyl-1,3-cyclohexadiene (31) were 50% and 70%, respectively. As a control it was determined that 1-vinylcyclohexene (28) could be separated from all observed products, and a yield of 0.5% would have been easily detected.

Spectroscopic data. **1,2-Dimethylenecyclohexane (35):** ^1H NMR[31] ($CDCl_3$) δ 1.60–1.70 (m, 4 H, C3-H, C4-H), 2.20–2.35 (m, 4 H, C2-H, C5-H), 4.65 (d, 2 H, J_d = 1.7 H, exterior olefinic CH), 4.95 (d, 2 H, J_d = 1.7 H, interior olefinic CH); ^{13}C NMR[32,33] ($CDCl_3$) 28.0 (CH_2), 36.0 (CH_2), 108.0 (olefinic CH_2), 150.0 (olefinic C); MS *m/e* (relative intensity) 109 (5.5), 108 (P, 62), 93 (98), 91 (76), 80 (31), 79 (100), 78 (20), 77 (80), 67 (18), 65 (26), 53 (16), 52 (16), 51 (23). **1-Methyl-1,3-cycloheptadiene (30):** ^1H NMR[29,34] ($CDCl_3$) δ 1.80–1.95 (m, 2 H, C6-H), 1.80 (s, 3 H, CH_3), 2.25–2.35 (m, 4 H, C5-H, C7-H), 5.50–5.80 (m, 3 H, olefinic CH); ^{13}C NMR ($CDCl_3$) δ 26.0, 27.2, 32.0, 37.0, 121.0, 125.0, 132.0, 143; MS *m/e* (relative intensity) 109 (3.4), 108 (P, 39), 93 (100), 91 (70), 80 (26), 79 (59), 78 (16), 77 (69), 65 (18). **2-Methyl-1,3-cycloheptadiene (31):** ^1H NMR[34] ($CDCl_3$) δ 1.75–1.95 (m, 2 H, C6-H), 1.78 (d, 3 H, J_d = 6 Hz, CH_3), 2.20–2.40 (m, 4 H, C5-H, C7-H), 5.60–5.90 (m, 3 H, olefinic CH); ^{13}C NMR ($CDCl_3$) δ 26.2, 27.2, 30.0, 32.0, 128.6, 129.5, 132.2, 132.9; MS *m/e* (relative intensity) 109 (3.3), 108 (P, 38), 93 (100), 91 (67), 80 (19), 79 (42), 77 (56). **5-Methyl-1,3-heptadiene (32) and 6-methyl-1,3-heptadiene (33):** ^1H NMR[35-38] ($CDCl_3$) δ 1.49 (d, 3 H, J_d = 6.5 Hz, CH_3 of 6-methyl isomer), 1.56 (d, 3 H, J_d = 7.4 Hz, CH_3 of 5-methyl isomer), 1.60–1.85, 2.00–2.20, 2.30–2.40, 2.50–2.60 (m, 10 H, CH_2 groups of both isomers), 5.60–5.90 (m, 8 H, olefinic CH of both isomers); ^{13}C NMR ($CDCl_3$) δ 22.0, 22.5, 29.0, 32.0, 33.0, 36.0, 40.0, 123.0, 125.0, 125.5, 132.0, 134.0, 140.0; MS[37] *m/e* (relative intensity) 109 (3.8), 108 (P, 44), 93 (88), 91 (79), 80 (31), 79 (100), 78 (24), 77 (83), 66 (16), 65 (24), 51 (16).

Pyrolysis of the Sodium Salt of 1,5-Cyclohexadiene-1-carboxaldehyde Tosylhydrazone (38). The procedure was similar to that for the pyrolysis of the sodium salt of 1-cyclohexene-1-carboxaldehyde tosylhydrazone described above: 1.81 mmol of sodium salt were pyrolized, assuming quantitative conversion of the tosylhydrazone to its sodium salt. The initial pressure was 6 μm, and the pyrolysis zone was heated to 540 °C. The reservoir was heated from 0 to 108 °C over 98 min, and the pressure rose to a maximum of 45 μm before returning to 6.5 μm. The conversion of starting sodium salt was 50.1%. Only one volatile product was detected by gas chromatography, 6,7-dihydro-1*H*-indazole (39), formed in 86.8% yield: ^1H NMR[39] ($CDCl_3$) δ 2.30–2.50 (m, 2 H, C6-H), 2.85 (t, 2 H, J_t = 8.3 Hz, C7-H), 5.69 (dt, 1 H, J_d = 9.9 Hz, J_t = 4.6 Hz, C5-H), 6.41 (dt, 1 H, J_d = 9.0 Hz, J_t = 2.1 Hz, C4-H), 7.30 s, 1 H, C3-H); ^{13}C NMR ($CDCl_3$) δ 21.0, 24.0, 116.0, 120.0, 124.0, 126.0, 147.0; MS *m/e* (relative intensity) 121 (1.3), 120 (P, 12), 119 (30), 118 (100), 92 (16), 91 (95), 90 (24), 89 (22), 65 (23), 64 (48), 63 (77), 62 (40), 61 (21), 52 (32), 50 (18).

Acknowledgment. We are grateful to the National Science Foundation for support of this work under Grant No. CHE-88-02677. We thank Professor Curt Wentrup for helpful suggestions. We thank Janet Braddock Wilking, Dennis Moore, and Andrew Tyler for recording mass spectra at the Washington University Mass Spectrometry Resource, which is supported by National Institutes of Health Grant No. RR00954.

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